

COATINGS. ENAMELS

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POROUS COMPOSITE MATERIALS BASED ON LIQUID GLASS AND NATURAL SILICATES

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Composite materials based on sodium silicate, tremolite, diopside, wollastonite, and industrial waste (milled porcelain and fired clay powder) are synthesized. A technological scheme for their production is proposed.

The development and use of new promising materials is an important factor in solving economic problems, which include the shortage of natural resources, the shortage of strategic materials, and the necessity of keeping up the economic growth rate and competitiveness in the world market. The use of promising materials makes it possible to lower the production cost and to organize flexible production in the market economy. Such materials primarily include porous inorganic materials with an extended macrostructure that have multiple purposes.

The aim of the present study was to obtain highly porous composite materials resistant to aggressive media based on alkaline and natural silicates (foam silicates). Such materials developed on the basis of various colloid and microheterogeneous forms of silica are suitable for construction of residential, administrative, and industrial buildings [1, 2]. Their application makes it possible to decrease the thickness of fencing structures, which lowers the construction and maintenance costs. An advantage of these materials is primarily their inorganic composition; consequently, they are resistant to various microorganisms and do not release toxic compounds in the course of service. On the other hand, their source materials are quartz sand, soda, construction material waste, and waste generated at ceramic and porcelain factories, which ensures environmentally safe production, contributes to decreasing the production cost, and facilitates their wide application.

We have developed a technological scheme for producing such materials including the synthesis of impure sodium disilicate, dissolving in an autoclave, producing sodium silicate solution (liquid glass), introducing a filling agent, pro-

ducing granules in the presence of a curing agent, heat treatment, drying at a temperature of 160–200°C, and foaming of the material at 300–400°C.

Porous materials were produced using liquid glass with a silicate modulus of 2.5 acting as the binding agent. The curing agent was CaCl_2 solution and the fillers belonged to the group of magnesium silicates: tremolite from the Alguiskoe deposit, diopside from the Aidanskoe deposit, wollastonite, and also industrial waste (milled porcelain and fired clay powder). The fillers were introduced in the amount of 10–30 wt. %

The choice of natural silicates as the fillers was based on the following assumptions [3]: introduction of initially water-resistant silicates improves the properties of the solidified material; non-water-resistant additives (both initial and products of hydrolysis) may penetrate and be distributed in the voids of the crystalline structure and the microstructure of the high-dispersion silicate material; the possibility of a chemical reaction of the product of solidification existing in a metastable state with the defective surface of the silicate material is not excluded.

To study the physiochemical processes in the formation of composite materials, the viscosity and conductivity of the solutions were determined using VPZh-2 and VPZh-4 viscosimeters and an instrument for measuring electric resistance. The thermal analysis was carried out on a Q-1500 derivatograph in the temperature range of 17–800°C in the air atmosphere. The IR spectra of the initial materials and samples were registered on a Spekord 75 spectrophotometer in the range of 4000–200 cm^{-1} . The acid-base properties were studied using the standard method. The salt of some *d*-elements were used to tint the material.

The study of the liquid-phase system indicated that the

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TABLE 1

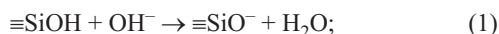
Composition of composite materials	Frequency of absorption spectrum maxima, cm ⁻¹	Correlation with silicate structures
Liquid glass, diopside, and porcelain powder	520, 645, 670, 1014, 930, 1190	Vibrations of tetrahedra [SiO ₄] ⁻ , pyroxene chains of diopside [SiO ₃] _∞
Liquid glass, diopside, and wollastonite	470, 510, 520, 640, 645, 670, 925, 1025, 1050, 1190	Vibrations of tetrahedra [SiO ₄] ⁻ , pyroxene chains of wollastonite [(SiO ₃) ₃] _∞
Liquid glass, wollastonite, tremolite, and porcelain powder	470, 545, 645, 750, 920, 980, 1025, 1070	Vibrations of tetrahedra [SiO ₄] ⁻ , ribbons of amphiboles [Si ₄ O ₁₁] _∞

TABLE 2

Composition of liquid glass – filler system	Metal ions introduced for tinting	Solubility in 0.1 M HCl, NaOH	Compressive strength, MPa	Color of materials
Diopside and porcelain powder	Cr ²⁺	Insoluble	1.44	Bright yellow
Diopside and wollastonite	Co ²⁺	The same	1.57	Sky-blue
Wollastonite, tremolite, and porcelain powder	Ni ²⁺	"	2.03	Light green
Tremolite	–	Soluble	0.57	White
Diopside	–	The same	0.37	The same
Wollastonite	–	"	0.40	Light gray

chemical reaction in the system is described by acid-base reactions:

the formation of ionic forms of silica:

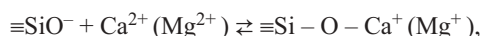


the polymerization reaction, which leads to the formation of polysilicates:



Reactions (1) and (2) are interrelated. The polymers formed according to reaction (2) do not have a linear but mostly a spherical structure. Colloid particles with the negative charge are formed in the course of polymerization [4].

When the fillers are added to the liquid-glass system, its viscosity sharply increases. Since the fillers include Ca²⁺ and Mg²⁺ ions, which react with the ionic forms of liquid glass according to the reaction



and the particles are fully or partly recharged, the colloid particles become enlarged and subsequently coagulate.

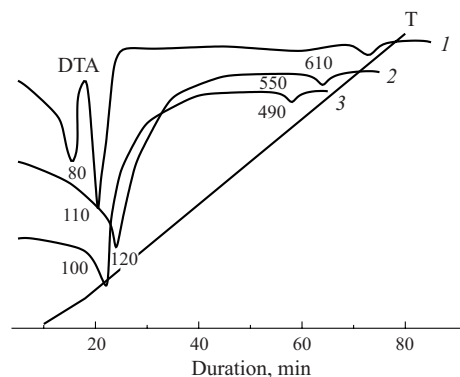
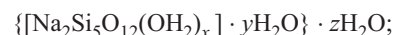


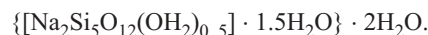
Fig. 1. Thermograms of liquid glass: 1) Liquid glass without dilution; 2 and 3) liquid glass diluted to 50 and 90%, respectively.

It is established that the formation of sodium silicate occurs in three stages (Fig. 1). At the first stage, adsorption water contained in the external coordination sphere evaporates; at the second stage, water contained in the inner coordination sphere is removed. At a higher temperature, hydrate water is released and sodium silicate becomes completely dehydrated.

As a consequence of performed studies, the amount of water in liquid glass contained in different coordination spheres is determined:



where $x + y + z = 4$, $x = 0.5$, $y = 1.5$, $z = 2.0$, i.e.,



The thermograms of the liquid-glass system diluted in water (Fig. 1) exhibit two endothermic effect. This is related to the fact that when liquid glass is diluted, the absorption water contained both in the inner and the outer coordination sphere is removed without separating.

The IR spectra were registered to interpret the structures of the obtained samples. The IR spectroscopic analysis data (Table 1) confirmed the existence of groups [SiO₄]⁴⁻ in the structures. It is established that adhesion is mainly due to the formation of pyroxene chains, which are typical of wollastonite and diopside, and amphibole ribbons typical of tremolite.

Due to the cementing adhesion of the binding fillers to the defective structure of the silicate component and its macrostructure, high strength of solidified material is ensured.

The properties of the obtained materials are given in Table 2. The complex composites, which contain more than two components introduced as fillers, have higher hardness, chemical resistance, and better tinting parameters. Such materials are insoluble in water.

There are currently various approaches to clarify the relationship between the properties of elements and the crystallochemical structure of a material. According to the data in [5], the acid-base properties of components play a

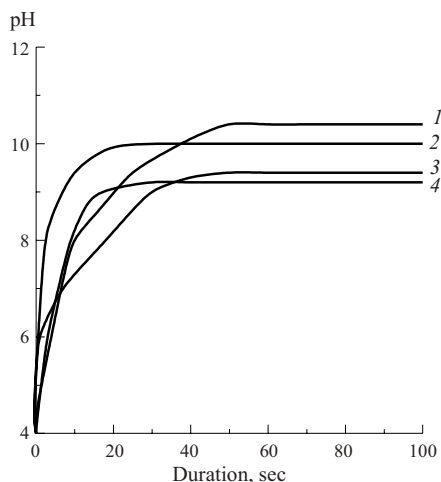


Fig. 2. Acid-base properties of materials: 1) diopside; 2) tremolite; 3) wollastonite; 4) composite material based on liquid glass, diopside, and porcelain powder.

great role in determining the structural types of crystalline compounds. Therefore, we investigated the acid-based properties of the obtained materials and fillers (Fig. 2). The composite material based on liquid glass, diopside, and por-

celain powder has more expressed acid properties and is more resistance to aggressive media. The resistance of acid complexes is primarily due to the oriented type of covalent bonds in them and significantly lower stability of the polyhedra around the cations with the base properties (a consequence of non-oriented ionic electrostatic bonds) [5].

Thus, composite materials based on sodium silicate, tremolite, diopside, wollastonite, and industrial waste (milled porcelain and fired clay powder) can be used for the production of protective and decorative coating and foam silicates.

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